Chemical Engineering Journal 158 (2010) 482–488

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

A comparative study between photocatalytic and photoelectrocatalytic properties of Pt deposited TiO_2 thin films for glucose degradation

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ARTICLE INFO

Article history:
Received 14 August 2009
Received in revised form 10 January 2010
Accepted 13 January 2010

Keywords:
Platinum
Titanium dioxide
Photocatalysis
Photoelectrocatalysis
Glucose

ABSTRACT

This study compares the photocatalytic (PC) and photoelectrocatalytic (PEC) oxidation of glucose by Pt–TiO_2 films under similar conditions. The overall oxidation efficiency of the PEC process was better than the PC process, for both TiO_2 and Pt–TiO_2 films. The Pt deposits enhanced the PEC oxidation efficiency of glucose at low cathodic (−0.1 V) and low anodic potential bias (+0.1 V). As the applied anodic bias was increased to >+0.5 V, the undoped-TiO_2 films outperformed their Pt–TiO_2 counterparts. This suggests that in the studied systems, at an anodic bias of >+0.5 V, more holes were available for the oxidation of glucose on the surface of TiO_2 compared to Pt–TiO_2 films. In the PEC systems, above a certain applied bias, Pt deposits may have a detrimental effect on the performance of a PEC system because the Pt deposits could merely block the surface of TiO_2 (particularly at the highest Pt loadings). Lower measured photocurrents from Pt–TiO_2 films compared to undoped-TiO_2 and a decrease in the photocurrent as the Pt loading increased corroborate this postulation.

1. Introduction

The titanium dioxide photocatalysis process has been investigated rigorously for the remediation of contaminated water and air [1–3]. Surface metallization of TiO_2 by the photodeposition technique is most commonly used to improve the quantum efficiency of the process [4–12], which would otherwise be limited to the order of 1% or less due to rapid electron–hole recombination. The use of the electrochemical approach to enhance the photocatalytic process has been demonstrated to improve the quantum efficiency of such a light driven process [13–18]. The application of an anodic bias directs most of the photogenerated electrons away from the conduction band of TiO_2, hence lowering electron–hole recombination events and promoting hole transfer to organic contaminants at the interface.

To date, most TiO_2 surface platinization has been on TiO_2 particles for slurry-type photocatalytic systems rather than on TiO_2 thin films. The effect of Pt deposition on TiO_2 photocatalysis has been reported to vary, and has been found to depend on the pollutant that is being degraded [5,19]. When a beneficial effect of Pt is observed, it is frequently proposed that the establishment of a space charge layer at the Pt–TiO_2 junction accelerates the removal of photoelectrons from the semiconductor and their transfer to oxygen or other electron acceptors in the solution [4,20,21]. This is said to not only decrease the incidence of photogenerated electron–hole recombination [22], but also to promote the reduction of oxygen, which has been identified as a possible rate-limiting step in the photocatalytic oxidation of some organics [23]. Additionally, the performance enhancement of Pt deposits has also been attributed to the dark catalysis displayed by Pt–TiO_2 [14], which could potentially be via dehydrogenation [4], oxidative dehydrogenation or hydrolysis by the Pt deposits [5]. As our recent work illustrated [5], the influence of the Pt deposition is governed by the nature of the organics being oxidized. The effects of TiO_2 platinization could also depend on the oxidation state of the photodeposited Pt [9]. Lee and Choi reported Pt^0 as the most active oxidation state of the Pt deposits [9], while Teoh et al. found that there is an intricate interrelationship between the Pt oxidation state and the degradation pathway of the organic compound [7].

Studies on Pt–TiO_2 thin films for photoelectrocatalysis processes are limited [14,24,25] and implications thereof are not fully known nor understood. A direct extrapolation of findings from Pt platinization of TiO_2 powders to thin film photocatalysis or thin photoelectrocatalysis cannot be drawn, as the charge carrier dynamics are rather different. It is well known that charge transport, consumption and recombination processes are important attributes that determine the kinetics, efficiency and reaction pathway of a photocatalytic degradation process. In these regards,

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doi:10.1016/j.cej.2010.01.030

a PC process differs remarkably from a PEC process. In a PC process, both oxidation and reduction half reactions occur at different locations on the same TiO_2 crystals/particles. The reduction half reaction relies purely on the presence of molecular oxygen or other electron acceptors to remove the photogenerated electrons from the conduction band. This is often a limiting step of the overall reaction due to the low concentration of available electron acceptors near the surface. Under such circumstances, surface deposited Pt could act as a 'catalyst' to facilitate the photoelectron consumption or the reduction half reaction, leading to an enhanced overall efficiency. In case of a PEC process, the oxidation and reduction half reactions occur separately at the anode and cathode, respectively. This physical separation of oxidation and reduction half reactions in addition to an appropriate applied potential bias makes a PEC process independent of electron acceptor concentration [26,27]. This is because the applied potential bias serves as an external driving force to remove the photogenerated electrons from the conduction band to the external circuit then to the auxiliary electrode (cathode) where the forced reduction half reactions take place. In other words, photoelectron consumption in a PEC process is very different to that of a PC process. For this reason, the role of deposited Pt on a TiO_2 surface in a PEC process could be different to that of a PC process.

When comparing the Pt platinization of TiO_2 powders to thin film photocatalysis or thin photoelectrocatalysis, there are other differences that need to be highlighted. When TiO_2 powders are suspended in an aqueous suspension, charge carrier recombination occurs on the surface or in the bulk of one TiO_2 particle (alternatively, this could involve a few TiO_2 particles if agglomerates are present). However, in the case of TiO_2 films, charge carriers migrate throughout the whole film. This process involves multi-grain interfacial transfers. Therefore, electron–hole recombination in films is expected to be greater in TiO_2 films due to multi-recombination within grain volumes and at grain interfaces. Hence, the photoactivity of TiO_2 films is often influenced by 2 important parameters, film thickness and film porosity [28]. Finally, He et al. [14] showed that differences in preparation methods of Pt deposited TiO_2 can also lead to differences in film properties (when compared to powders), possibly manifesting themselves as variations in Pt deposit size. Such differences can lead to differences in mechanisms (dark catalytic combined with photoelectrochemical in films) as opposed to only photoelectrochemical in powders dip-coated as films.

In this context, a comparative study of PC and PEC degradation processes under comparable conditions would be of scientific and practical interest, as it would allow for a better understanding of the mechanistic role of deposited Pt in PC and PEC processes. To ensure the experimental conditions are comparable, both PC and PEC experiments were carried out using the same thin-layer photo(electrochemical)-catalytic system, consisting of a reaction cell and a detection cell. A series of Pt–TiO_2 films with varying amounts of Pt deposits were prepared and tested for the oxidation of glucose. The oxidation efficiencies were compared and analyzed as a function of surface Pt content, applied potential bias and glucose concentration.

2. Materials and methods

2.1. Materials

Indium tin oxide (ITO) conducting glass slides were purchased from Delta Technologies Ltd. (USA). Hexachloroplatinic acid (99%, Unilab), titanium (IV) tetraisopropoxide (97%, Aldrich), isopropanol (99.5%, Ajax), glucose (99%, BHD) and $NaClO_4$ (Ajax) were used as received. Milli-Q water (Millipore, Milli-Q Plus) was used for preparing all solutions. The pH of the solution was adjusted either with NaOH or $HClO_4$.

2.2. Preparation and characterization of Pt–TiO_2 films

A TiO_2 sol was prepared according to the method by Day et al. [29]. Titanium tetraisopropoxide, TTIP was hydrolyzed with a 0.5 equiv. of water in isopropanol at ambient temperature. The mixture was then refluxed at 78 °C for 20 h to yield a transparent sol. The sol was deposited on the ITO glass substrates (75 mm × 15 mm × 1 mm) by using a dipping unit. The substrates were dip-coated once for 30 s and lifted out of the dipping solution at a speed of $2.3\,\mathrm{mm\,s^{-1}}$. The coated slides were dried in air and then annealed in a muffle furnace at 450 °C for 30 min. Platinum was deposited on TiO_2 films photochemically from a hexachloroplatinic acid solution, H_2PtCl_6 (pH 3) in the presence of 0.05 M of oxalic acid. By adjusting the concentration of hexachloroplatinic acid solution from 0.1 to 1.0 mM, the amount of platinum deposited was varied. The Pt–TiO_2 films prepared were identified by the platinum ion loading added to the solution prior to illumination.

The morphology of the TiO_2 films was observed using Transmission Electron Microscopy (TEM, Phillips CM-200) at an accelerating voltage of 200 kV. The phase content of the TiO_2 film coated on ITO glass was analyzed by a Philips X'Pert MRD X-ray diffractometer, using graphite monochromatic copper radiation (Cu-Kα) at 45 kV, 40 mA over the 2θ range of 20–80°. A surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB220iXL) using an Al-Kα source (1486.6) in an ultra high vacuum chamber (25×10^{-10} mbar). Photoelectrons were collected by a hemispherical analyzer at 90° take-off angles. The spectra were calibrated with the C1s peak at 284.7 eV.

2.3. Photocatalytic and photoelectrocatalytic tests

PC and PEC experiments were carried out in batch mode in the reaction cell of a serial thin-layer photo(electrochemical)-catalytic system, as shown in Fig. 1. The reaction cell thickness was 0.25 mm, the illumination area was $489\,\mathrm{mm^2}$ and the cell volume was $160\,\mathrm{mm^3}$. For the PEC experiments, a platinum disc was used as the counter electrode. The illumination source for the reaction cell was a UV-LED array which consisted of 4 pieces of UV-LED (NCCU033(T), Nichia Corporation). The specified peak wavelength of the UV-LED was 365 nm and the spectrum half width was 8 nm. The UV-LED array optical outputs were adjusted by a power supply. The UV intensity impinging on the electrode surface was measured to be $25\,\mathrm{mW\,cm^{-2}}$ using an UV-irradiance meter (UV-A, Beijing Normal University). Prior to illumination, the reaction cell was filled with the reaction solution with a known concentration of glucose in a supporting electrolyte (2.0 M $NaClO_4$). The pH of the solution was approximately 6. The oxidation of glucose was initiated by illuminating the cell. Typically, the reaction took 20 min for completion. The exit solution from the reaction cell was subsequently pumped to a down-stream detection cell. The operation of the detection cell was based on an exhaustive PEC degradation process, PECOD method. This method integrates the photocurrent originating from the photocatalytic oxidation of organic compounds to quantify the extent of degradation. Details on the design and operation of the detection cell can be found in previous works [26,30]. A potentiostat (Model 362, Princeton Applied Research) was used to apply potential bias in reaction and detection cells. Potential and current signals were recorded using a computer coupled with a data acquizition system (e-corder, eDAQ Pty. Ltd.).

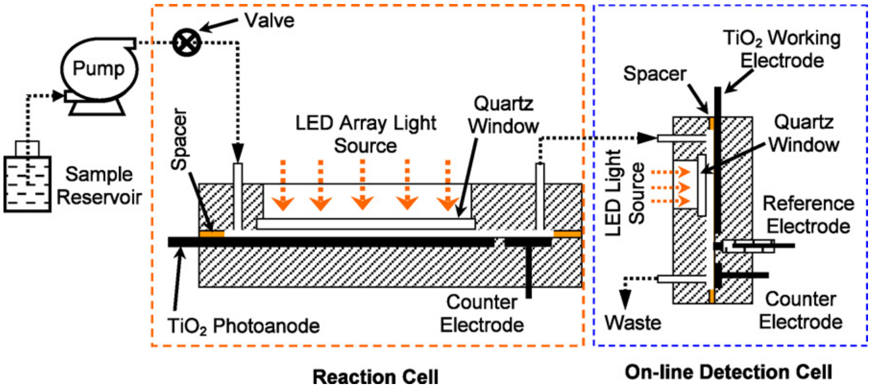

Fig. 1. Schematic diagram of the serial thin-layer photo(electrochemical)-catalytic degradation system with a UV-LED array.

2.4. Photoelectrochemical measurements

Linear sweep voltammograms (LSV) were obtained in a three-electrode electrochemical cell containing 100 cm^3 of 0.1 M $NaClO_4$ as supporting electrolyte with a quartz window for illumination. The exposed area of working TiO_2 or Pt–TiO_2 electrodes for photoelectrochemical reactions was 0.79 cm^2. A saturated Ag/AgCl electrode and a platinum plate were used as the reference and the auxiliary electrodes, respectively. The pH of the solution was adjusted to pH 6 at the beginning of all experiments. UV illumination was provided using 150 W Xenon arc lamp light source and focusing lenses (Beijing Optical Instruments) in conjunction with a UV band pass filter (UG-5, Schott). This assembly provided UV irradiation in 230–400 nm at intensity of 6.6 mW cm^{-2}, as measured with a UV-irradiance meter (UV-A, Beijing Normal University).

3. Results and discussion

3.1. Chemical composition of Pt deposits

Fig. 2 shows the TEM micrograph of a typical TiO_2 film prepared by the dipping method as described earlier. Here, the lattice fringe is clearly evident, signifying the high crystallinity of the deposited TiO_2 film. The XRD analysis showed that the TiO_2 film consisted of anatase. Peaks corresponding to rutile and brookite were not observed.

As mentioned earlier, Pt was deposited photochemically onto the TiO_2 films. Fig. 3 shows XPS spectra for the platinized TiO_2 film obtained using 1.0 mM H_2PtCl_6 solution in the platinum (Pt4f), titanium (Ti2p) and oxygen (O1s) regions (70–79, 455–465 and 529–533 eV, respectively). In the platinum region, the spectrum could be deconvoluted into three pairs of doublets. The Pt4f$_{7/2}$ and Pt4f$_{5/2}$ peaks at 70.33 and 70.93 eV; 73.36 and 73.94 eV, respectively, were attributed to atomic state Pt(0), while the third pair at ca. 72.72 and 75.93 eV corresponded to the oxidation states of Pt(II). The peak values agree fairly well with previously published data [31,32]. By comparing the normalized peak areas, Pt(0) was found to be the dominant species (~90%). The Pt(II) group (~10%) could be attributed to the presence of PtO and $Pt(OH)_2$ on the film surface since oxygen has a high tendency to chemisorb on the clean platinum surface during storage under ambient conditions and oxidize the Pt species [33]. The titanium peak at 458.90 eV was used as the binding energy reference in this analysis (Fig. 3B). Fig. 3C shows the O1s spectrum centered at 529.86 eV. This is a characteristic peak for metal oxides and agrees with O1s electron binding energy for a TiO_2 molecule [34]. All other Pt–TiO_2 samples displayed similar XPS characteristics as the 1.0-mM Pt–TiO_2 sample presented here. From the normalized peak area, the surface loading of atomic Pt deposits (Pt(0):Ti atomic percentage) was quantified to be approximately 3.8%, 12.2% and 26.5% for the films prepared at 0.1, 0.5 and 1.0 mM H_2PtCl_6, respectively.

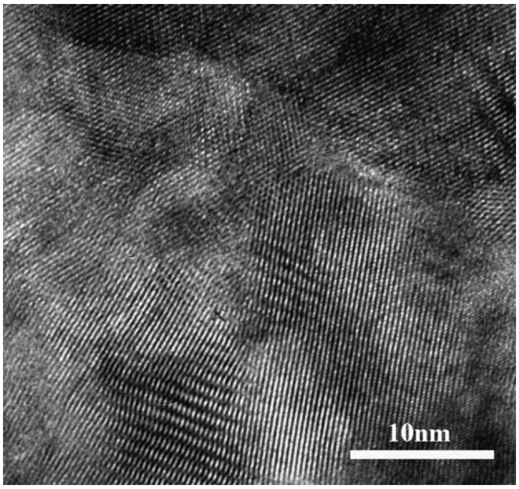

Fig. 2. TEM micrograph of a TiO_2 film prepared by the dipping method.

3.2. Photocatalytic performance

In Fig. 4, the results of the photocatalytic degradation experiments are presented. This figure shows the amount of glucose oxidized photocatalytically by TiO_2 and Pt–TiO_2 films under UV illumination using Pt–TiO_2 with various Pt loadings and at different initial glucose concentrations. At an initial glucose concentration of 0.05 mM 20% (0.0016 μmole) was mineralized by the undoped-TiO_2 film. For the same initial glucose concentration (0.05 M), Pt–TiO_2 films prepared using 0.1, 0.5 and 1.0 mM Pt solution oxidized 37% (0.003 μmole), 50% (0.004 μmole) and 28% (0.0022 μmole) of glucose, respectively. Hence, the Pt deposition on the TiO_2 films surface exhibited a net beneficial effect for the photocatalytic degradation of glucose. An optimum Pt loading was obtained with the 0.5-mM Pt–TiO_2 sample. There are several reasons for a decrease in the photocatalytic performance above an optimum loading and these have been discussed in the literature [35,36]. For example, it is noted that the 1.0-mM Pt–TiO_2 sample had a surface loading of 26.5% Pt, this high loading is believed to lead to UV shielding. Additionally, at higher Pt loadings, the Pt deposits occupy a significant number of the reactive surface sites, hence resulting in fewer reactive sites for the degradation of glucose. This was also suggested by Chen et al. [37] for Pt–TiO_2 photocatalytic systems when used for the generation of H_2 from methanol. An analogy is drawn here to Se–TiO_2 systems in which Se deposits

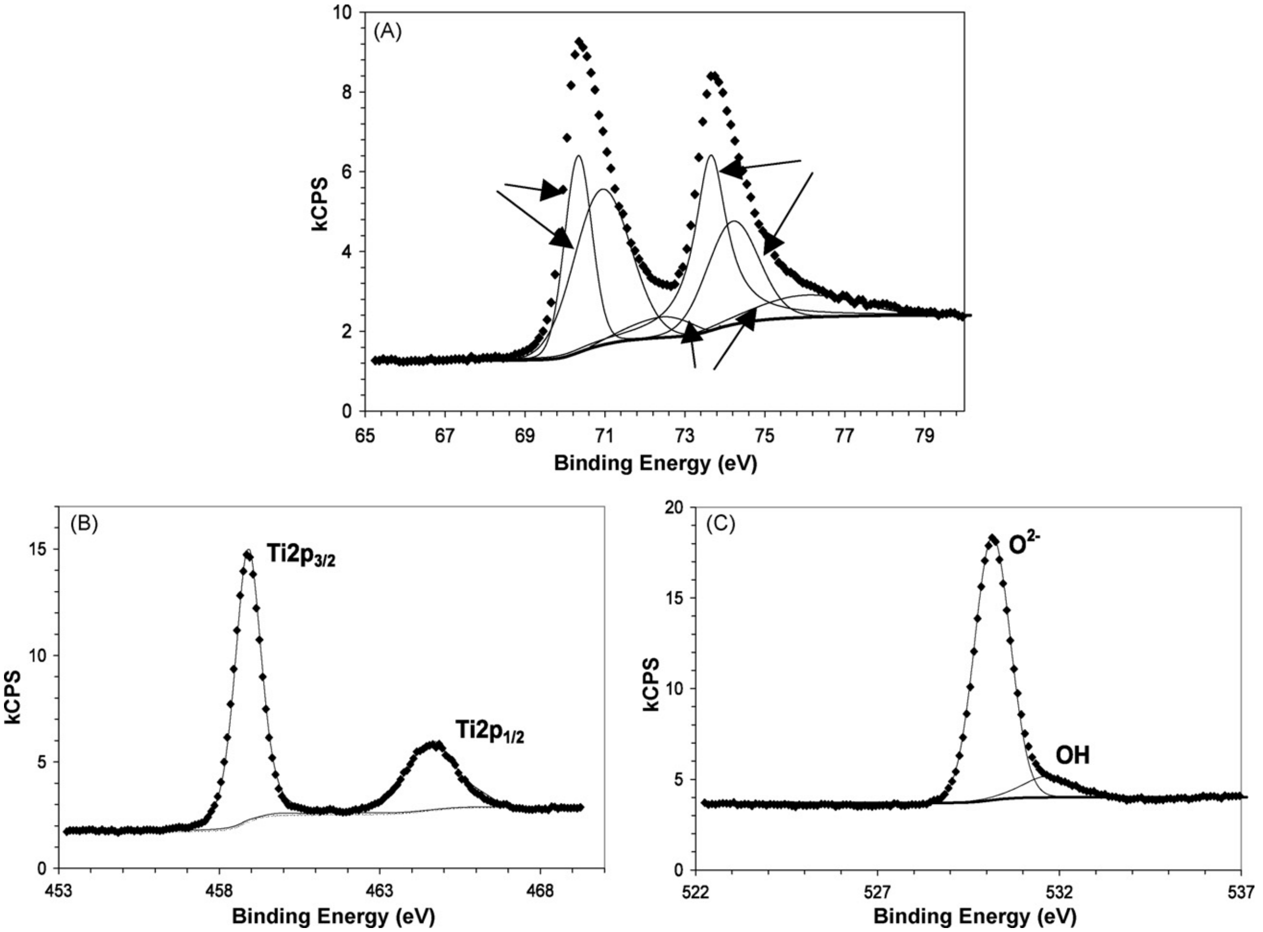

Fig. 3. XPS spectra of the 1.0-mM Pt–TiO_2 film and the corresponding assignment of XPS bands in the (A) platinum, (B) titanium and (C) oxygen [the data points show the experimental spectra and black lines show the deconvoluted spectra].

were shown to occur preferentially on the surface irregularities of TiO_2 that are believed to be more active [38].

As also shown in Fig. 4, as the initial concentration of glucose was increased to 0.1, 0.15 and 0.02 M, the presence of an optimum Pt loading was again observed. It can be seen here that the beneficial effect of platinum for the photocatalytic oxidation of glucose was greater at the higher glucose concentration. These results can be explained as follows: the rate of the photooxidation reaction is a function of the concentrations of organic and active species present in solution at a given time, as shown by Eq. (1), where [S*] is the concentration of active species, [C] is the concentration of organic substrate and $k_{reaction}$ is the rate constant [39]. The active species include photogenerated holes and electrons, hydroxyl radicals, and superoxide radicals:

$$\left(\frac{dCO_2}{dt}\right) = k_{reaction}[C][S*] \tag{1}$$

At low glucose loadings, it is believed that the concentration of active species ([S*]) is in excess of the glucose concentration ([C]) and the reaction rate is therefore not affected by [S*]. At higher glucose loadings, $[C] \gg [S^*]$, and the photooxidation reaction becomes limited by [S*]. Under these conditions, an increase in electron–hole recombination will result in a decrease in [S*], hence the rate of electron–hole recombination plays a significant role in determining the observed photooxidation rate of glucose [13,39].

3.3. Photoelectrocatalytic performance

Fig. 5 shows the photocurrent response of TiO_2 and Pt–TiO_2 films as a function of applied potential. The photocurrent of the films varied with applied potential and Pt content. In the absence of UV illumination, there was no measured current for all films (curve E). It is interesting to note that when applying a cathodic potential bias (i.e.,−0.1 V) or a small anodic potential bias (i.e., +0.1 V), the undoped-TiO_2 films showed an almost equal photocurrent to the 0.1-mM Pt–TiO_2 film, and when the applied potential bias was

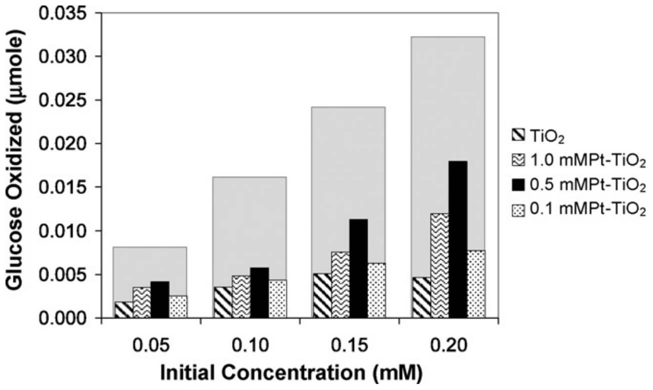

Fig. 4. Photocatalytic oxidation of glucose by TiO_2 and Pt–TiO_2 films at different initial concentrations of glucose [the grey area represents the initial amount of glucose; reaction time = 20 min; experimental volume = 160 μL].

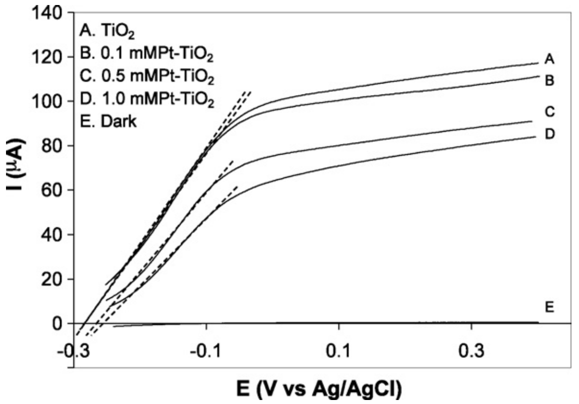

Fig. 5. Photocurrent response of (A) TiO_2, (B) 0.1-mM Pt–TiO_2, (C) 0.5-mM Pt–TiO_2, and (D) 1.0-mM Pt–TiO_2 films. The intersection of the dashed line on *x*-axis indicates the respective flatband potential.

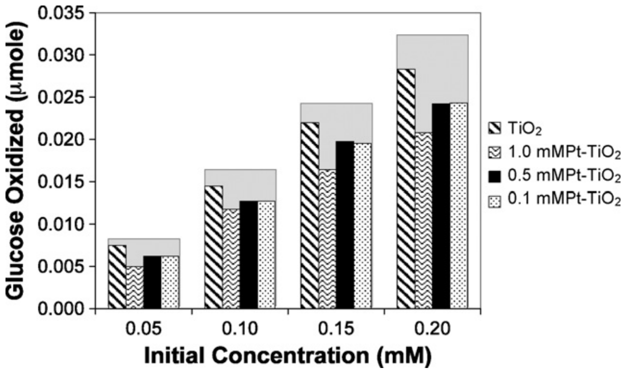

Fig. 7. Photoelectrocatalytic oxidation of glucose by TiO_2 and Pt–TiO_2 films at different initial concentrations of glucose [the grey area represents the initial amount of glucose; *E* = +0.9 V vs Ag/AgCl; reaction time = 20 min; experimental volume = 160 μL].

more positive than +0.5 V, the photocurrent in the undoped-TiO_2 superseded that of the Pt–TiO_2 films. Additionally, the resulting saturation current under a potential bias was found to decrease as the Pt content increased.

The flatband edge potentials can also be derived from Fig. 5. The method we used to derive the flatband potential is based on the measurement of the "on-set" potential. The applied potential bias to the photocatalyst anode serves the function of motive force to drive the electron movement inside the semiconductor photocatalyst layer. For a n-type semiconductor electrode, when the applied potential is below the conduction band edge (or below the flatband potential), there would be no electrons withdrawn from the semiconductor. As a result there is no anodic current observed. The on-set potential in this work refers to the potential at which anodic photocurrent begins to be measured. At these potentials, all the photogenerated charge carriers recombine without producing a net current flow [40,41]. As can be seen from Fig. 5, the apparent flatband potential of the TiO_2 film was −0.28 V (vs Ag/AgCl). The apparent flatband potentials for the 0.1-mM Pt–TiO_2, 0.5-mM Pt–TiO_2 and 1.0-mM Pt–TiO_2 films were −0.27, −0.26 and −0.24 V, respectively. This slight shift in potential with Pt deposition suggests surface energetic distribution changes by the deposited metal.

In the first set of PEC experiments, the effect of applied potential bias was investigated. Fig. 6 shows the amount of glucose oxidized by TiO_2 and Pt–TiO_2 films under applied potential bias ranging from −0.1 to +0.9 V (vs Ag/AgCl), while Fig. 7 shows the photoelectrocatalytic oxidation of glucose by TiO_2 and Pt–TiO_2 films at different initial concentrations of glucose at an applied anodic potential of +0.9 V. Firstly, from a comparison between the photocatalytic results presented in Fig. 4 with the photoelectrocatalytic results presented in Fig. 6, it is clear that higher glucose photooxidation efficiencies were achieved using the PEC system compared to the PC system, using both TiO_2 and Pt–TiO_2 films at an anodic bias of +0.9 V.

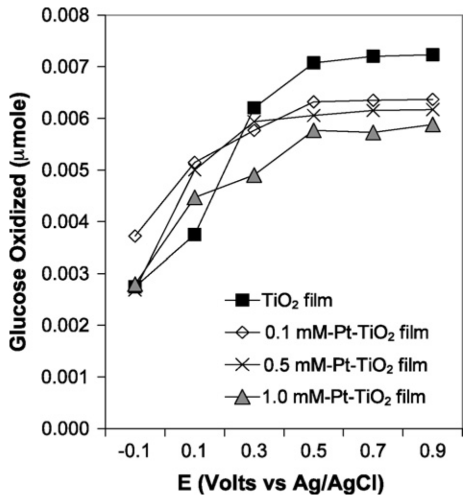

Fig. 6. Effect of applied potential bias on the PEC oxidation of 0.10 mM glucose on TiO_2 and Pt–TiO_2 films [reaction time = 20 min; experimental volume = 160 μL].

From Fig. 6, it can be seen that the highest extent of glucose oxidation occurred under anodic bias +0.5 V with the undoped-TiO_2 film. These conditions achieved 90% (0.015 μmole) glucose oxidation. The 0.1-mM Pt–TiO_2 films had the second highest efficiency, followed by 0.5-mM Pt–TiO_2 and 1.0-mM Pt–TiO_2 films. The use of the 1.0-mM Pt–TiO_2 film in the PEC cell achieved approximately 75% (0.013 μmole) glucose oxidation. From these results it is also clear that undoped-TiO_2 electrodes at times out-preformed Pt–TiO_2 electrodes depending on the applied potential bias.

At an applied cathodic potential bias of −0.1 V, the Pt–TiO_2 films displayed higher glucose oxidation efficiency than the undoped-TiO_2 films. This could be due to the electron reactions playing a bigger role in the indirect oxidation of organics under cathodic conditions (in reactions involving superoxide radicals for example) [25], particularly on the Pt–TiO_2 films given that they favour electron transfer to oxygen in solution. At a low anodic potential bias (+0.1 V), the Pt–TiO_2 films also outperformed their undoped-TiO_2 counterparts. Here, it is believed that under these anodic conditions, the hole driven oxidation reactions were favoured on the Pt–TiO_2 films. This is believed to be due to enhanced electron–hole separation brought about by the Pt deposits, which are able to transfer the photogenerated electrons away. The dark catalytic effects of the Pt deposits may have also played a role [14].

As the anodic potential bias increased further (+0.3 V and above), the undoped-TiO_2 films began to outperform the Pt–TiO_2 films. This could mean that under these conditions, more holes were available for the oxidation of glucose on the surface of TiO_2 than on the surface Pt–TiO_2 films. We postulate that at a higher anodic potential the oxidation of glucose was no longer limited by electron–hole recombination (since the anodic bias minimized electron accumulation), however it may have become limited by the generation of electrons and hole pairs which was greater in the undoped-TiO_2 films due to shielding of the TiO_2 surface by the Pt deposits [13,14]. The higher photocurrent in the undoped-TiO_2 and the decrease in photocurrents with increased Pt loading reaffirm this postulation.

It is noted that as the potential bias is increased to +0.5 V and greater, the oxidation efficiency plateaus. This can be explained by the fact that the potential bias provides an electromotive force that

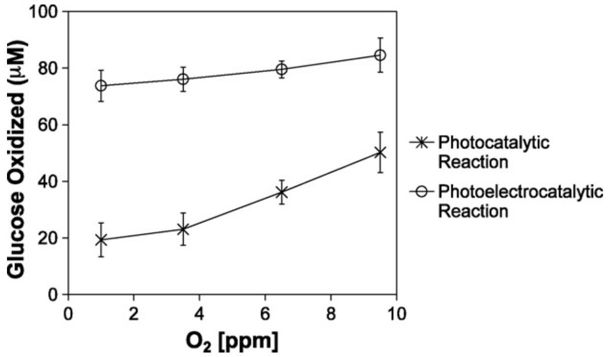

Fig. 8. Effect of O_2 concentration on the photocatalytic and PEC (+0.9 V vs Ag/AgCl) oxidation of 100 μM glucose by 0.5-mM Pt–TiO_2 film.

pulls the photogenerated electrons to the counter electrode, hence reducing charge carrier recombination and increasing the availability of active species. However, the number of active species that can be achieved in the TiO_2 or Pt–TiO_2 films is fixed, and it is because of this that after a certain anodic bias, the efficiency plateaus [13]. These findings are significant for application purposes, where optimum conditions for PEC systems need to be identified for either TiO_2 or Pt–TiO_2 films. Optimum PEC conditions could also be dependent on the nature of the organic that is being degraded and its redox potential.

Fig. 7 shows the amount of glucose oxidized at different initial glucose concentrations using TiO_2 and Pt–TiO_2 films in the PEC system. A potential bias of +0.9 V was applied for all runs. When comparing the degree of oxidation at different initial concentrations, the undoped-TiO_2 film had the highest PEC activity by oxidizing 90% (0.015 μmole) of the glucose initially present in the system. A slight detrimental effect in glucose oxidation was observed when using the Pt–TiO_2 films at all glucose concentrations compared to the undoped-TiO_2 films. As discussed earlier in Section 3.2, at the higher glucose concentrations the rate of oxidation of glucose is expected to be limited by the availability of active species (such as holes, hydroxyl radicals, superoxide radicals). The undoped-TiO_2 surface seems to provide more active sites than its Pt–TiO_2 film counterparts at the applied potential bias of +0.9 V. Among the platinized films, the 0.1-mM Pt–TiO_2 and 0.5-mM Pt–TiO_2 films had similar activities, while 1.0-mM Pt–TiO_2 film had the lowest activity. The presence of an optimum Pt loading was observed and explained earlier.

The effect of oxygen concentration on the efficiency of both the PC and PEC processes was also studied. In most cases, due to the limited amount of oxygen dissolved in the solution (<10 ppm at 25 °C, 1 atm), the interfacial oxygen reduction is the rate-limiting step of the overall photocatalytic reaction and therefore controls the efficiency of the system. This is evident in Fig. 8 which shows that the amount of glucose oxidized in the PC reaction increased significantly with an increase in dissolved oxygen concentration. In the case of the PEC system, oxidation of glucose was essentially independent of dissolved oxygen concentration. This reaffirms that at +0.9 V, the oxidation of glucose was predominantly hole driven as expected under anodic bias conditions.

4. Conclusion

The overall oxidation efficiency of the PEC process was better than the PC process, for both TiO_2 and Pt–TiO_2 films. At an applied cathodic potential bias, the Pt–TiO_2 films displayed higher glucose oxidation efficiency than the undoped-TiO_2 films. This could be due to the electron reactions playing a bigger role in the indirect oxidation of organics under cathodic conditions particularly on the Pt–TiO_2 films given that they favour electron transfer to oxygen in solution. At a low anodic potential bias (+0.1 V), the Pt–TiO_2 films also outperformed their undoped-TiO_2 counterparts. Here, it is believed that under these anodic conditions, the hole driven oxidation reactions were favoured on the Pt–TiO_2 films. This is believed to be due to enhanced electron–hole separation brought about by the Pt deposits, which are able to transfer the photogenerated electrons away. As the applied potential bias was increased further, the undoped-TiO_2 films showed higher photooxidation rates than the Pt–TiO_2 films. The Pt deposits may have had a detrimental effect since the Pt deposits may have blocked the surface of TiO_2, hence reducing the number of surface active sites (particularly at the highest Pt loadings). Lower measured photocurrents from Pt–TiO_2 films compared to undoped-TiO_2 and a decrease in the photocurrent as the Pt loading increased corroborate this postulation.

Acknowledgments

The authors thank Australian Research Council Nanotechnology Network for awarding Mr Wee Yong Gan the Long Term Visit funding to carry out this work at Griffith University, Gold Coast. This work was carried out with the financial assistance of the Australian Research Council Centre of Excellence for Functional Nanomaterials.

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